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Abstract - The solid-state structures of $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ (I) and $(\text{Me}_3\text{SiCH}_2)\text{InCl}_2$ (II) have been determined by single-crystal X-ray analysis. Compound I crystallizes as a centrosymmetric dimer, $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$, in the triclinic space group $P1 [(C_i^1)$, No.2] with unit cell parameters of $a = 10.682(1) \text{ \AA}$, $b = 12.441(1) \text{ \AA}$, $c = 6.141(1) \text{ \AA}$, $\alpha = 96.21(1)^\circ$, $\beta = 94.86(1)^\circ$, $\gamma = 75.04(1)^\circ$, $V = 782.4(2) \text{ \AA}^3$, and $D_{\text{calcd}} = 1.378 \text{ g cm}^{-3}$ for $Z = 1$ [$R = 0.072$ ($R_w = 0.098$)]. Compound II crystallizes as an infinite polymer, $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$, in the triclinic space group $P1 [(C_i^1)$, No.2] with unit cell parameters of $a = 6.708(6) \text{ \AA}$, $b = 12.771(11) \text{ \AA}$, $c = 6.553(5) \text{ \AA}$, $\alpha = 96.68(2)^\circ$, $\beta = 116.38(2)^\circ$, $\gamma = 95.56(2)^\circ$, $V = 492(1) \text{ \AA}^3$, and $D_{\text{calcd}} = 1.841 \text{ g cm}^{-3}$ for $Z = 2$ [$R = 0.036$ ($R_w = 0.036$)]. The geometry about each indium atom in II is trigonal bipyramidal.

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**X-RAY CRYSTAL STRUCTURES OF
[(Me₃SiCH₂)₂InCl]₂ and [(Me₃SiCH₂)InCl₂]_∞**

by

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X-Ray Crystal Structures of $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$ and $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$

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Abstract - The solid-state structures of $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ (I) and $(\text{Me}_3\text{SiCH}_2)\text{InCl}_2$ (II) have been determined by single-crystal X-ray analysis. Compound I crystallizes as a centrosymmetric dimer, $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$, in the triclinic space group $P1 [(C_i^1)$, No.2] with unit cell parameters of $a = 10.682(1) \text{ \AA}$, $b = 12.441(1) \text{ \AA}$, $c = 6.141(1) \text{ \AA}$, $\alpha = 96.21(1)^\circ$, $\beta = 94.86(1)^\circ$, $\gamma = 75.04(1)^\circ$, $V = 782.4(2) \text{ \AA}^3$, and $D_{\text{calcd}} = 1.378 \text{ g cm}^{-3}$ for $Z = 1$ [$R = 0.072$ ($R_w = 0.098$)]. Compound II crystallizes as an infinite polymer, $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$, in the triclinic space group $P1 [(C_i^1)$, No.2] with unit cell parameters of $a = 6.708(6) \text{ \AA}$, $b = 12.771(11) \text{ \AA}$, $c = 6.553(5) \text{ \AA}$, $\alpha = 96.68(2)^\circ$, $\beta = 116.38(2)^\circ$, $\gamma = 95.56(2)^\circ$, $V = 492(1) \text{ \AA}^3$, and $D_{\text{calcd}} = 1.841 \text{ g cm}^{-3}$ for $Z = 2$ [$R = 0.036$ ($R_w = 0.036$)]. The geometry about each indium atom in II is trigonal bipyramidal.

The use of alternative group 13 and group 15 compounds to fabricate traditional 13-15 materials has received great attention over the past decade. Indeed, fundamental chemistry involving the structure, bonding,

and reactivity of such species has been of primary concern in our laboratory for some time.¹⁻⁶ It is our belief, that through these investigations a better understanding can be obtained as to the factors that influence and dictate the reactivity of these species. Herein we report the solid-state structures of $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$ (I) and $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$ (II) which have been found to be dimeric and polymeric, respectively.

EXPERIMENTAL

Synthesis

All manipulations were performed using general Schlenk, Dry box (Vacuum/Atmospheres HE-493 Dri-Lab containing an argon atmosphere), or high vacuum techniques. Compounds I and II were isolated from the reaction of excess HCl with $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$ ⁷ and $[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$,³ respectively, and their mp's, ¹H NMR spectra, and elemental analyses (C and H) were in agreement with those of authentic samples prepared according to the procedure of Beachley *et al.*⁸ Crystals of I, suitable for X-ray analysis, were grown from pentane at -15° C. X-ray quality crystals of II were obtained by dissolving II in boiling chlorobenzene and cooling to room temperature.

X-ray structural solution and refinement

Crystallographic data for both I and II are summarized in Table 1. For compound I, the crystal used was a colorless block mounted inside a flame-sealed 0.6 mm thin-walled glass capillary under an inert argon atmosphere. Oscillation and Weissenberg photographs yielded preliminary unit cell parameters and space group information. X-ray intensity data were recorded at the Crystal Structure Center, Duke University, on an Enraf-Nonius CAD-4 diffractometer at 25° C using graphite-monochromated Cu-K α radiation ($\lambda =$

1.5418 Å). In addition to the usual Lorentz and polarization corrections a ψ -scan-derived empirical absorption correction ($T_{\max}:T_{\min} = 1.00:0.41$) was also applied. Laue symmetry indicated that the crystals belonged to the triclinic system, space group P1 or $P\bar{1}$; the latter was assumed at the outset and shown to be correct by the structure solution and refinement. The crystal structure was solved by the heavy-atom approach. Initial indium atom coordinates were derived from a Patterson map. The other non-hydrogen atoms were located in a series of weighted F_o and difference Fourier syntheses. Positional and thermal parameters (at first isotropic, then anisotropic) of these atoms were adjusted by means of several rounds of full-matrix least-squares calculations. Hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) in the later iterations which converged (max. shift/esd = 0.02) at $R = 0.064$ ($R_w = 0.087$). A final difference Fourier synthesis revealed no unusual features (max. 1.5, min. -1.3 e/Å³, both in the vicinity of the indium atom). Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package (SDP).⁹ For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 10. An ORTEP diagram showing the atom labeling scheme and solid-state conformation of I is presented in Figure 1.

For compound II, X-ray intensity data were collected at the Molecular Structure Center, Indiana University on a locally constructed diffractometer using an $\omega/2\theta$ scan technique with Mo K α radiation ($\lambda = 0.71073$ Å). A single crystal of II was affixed to the end of a glass fiber under an inert atmosphere of nitrogen and transferred to a goniostat which was cooled to -171°C under a flow of nitrogen. Cell parameters and an orientation matrix corresponded to a triclinic cell, space group P1 or $P\bar{1}$. Data were corrected for absorption, Lorentz and polarization effects, and averaged to yield a unique set of intensities. The structure was solved using a combination of direct methods

(MULTAN78) and Fourier techniques based on 1281 unique reflections with intensities $I > 3\sigma(I)$ in the range $6^\circ < 2\theta < 45^\circ$. Least-squares refinement converged at $R = 0.036$ ($R_w = 0.036$). Anisotropic thermal parameters were used for all non-hydrogen atoms. Some of the hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen positions; all hydrogens were included as fixed atom contributors in idealized positions for the final cycles of refinement. An ORTEP diagram showing the atom labeling scheme and solid-state conformation of **II** is presented in Figure 2.

Atomic coordinates, positional parameters, anisotropic thermal parameters, distances, angles, and observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

In accord with the degree of association in solution found by Beachley *et al.*,⁸ the solid-state structure of **I** consists of discrete chlorine bridged dimers lying on crystallographic centers of symmetry, and thus their In-Cl-In-Cl ring is strictly planar. The geometry at the indium atoms is considerably distorted tetrahedral, $\text{Cl-In-Cl}' = 84.8(1)^\circ$, $\text{Cl-In-C} = 101.0(3) - 104.3(3)^\circ$, and $\text{C11-In-C21} = 144.7(5)^\circ$. The very large exocyclic angle subtended at the indium atom is undoubtedly due to the substantial steric demands of the geminal Me_3SiCH_2 groups. In-C bond lengths of $2.11(1)\text{\AA}$ for both In-C11 and In-C21 lie within the $2.093(6)\text{\AA} - 2.26(2)\text{\AA}$ ¹¹ range of reported values. The mean In-Cl length of 2.617\AA also falls within the range of values for similar bridging systems.³

Due to the limited solubility of **II** in hydrocarbon solvents, Beachley *et al.*⁸ were unable to determine its degree of oligomerization through cryoscopic molecular weight determination. On the basis of IR and NMR data, however, they concluded that the solid-state structure of **II** probably consisted of

extensive associations through chlorine atom bridging.⁸ The X-ray crystallographic analysis reveals that the solid-state structure of $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$ (II) consists of a theoretically infinite chain of five-coordinate indium atoms in a one-dimensional polymer. This polymeric chain is achieved through bridging by the chlorine atoms to form In-Cl-In-Cl rings. The geometry about the indium atoms is distorted trigonal-bipyramidal with bridging chlorine atoms situated at the axial sites while equatorial positions are occupied by two chlorine atoms bridging two different metal centers and one Me_3SiCH_2 group. The axially disposed chlorine atoms are almost equally displaced ($\Delta = 2.677, 2.694 \text{ \AA}$) from the least-squares plane through In1, C4, Cl2, and Cl3. The Me_3SiCH_2 groups alternate on either side of the $[\text{In}(\mu\text{-Cl})_2]_\infty$ chain resulting in a stair-step polymer. A similar situation was encountered in the neopentyl analogue, $[(\text{Me}_3\text{CCH}_2)\text{InCl}_2]_\infty$ (III)¹² and $[\text{MesInI}_2]_\infty$ (IV).¹¹ As was observed for III, the In-Cl bond distances involving the axial chlorine atoms in II are significantly longer [mean $\text{In-Cl}_{(\text{axial})} = 2.715$ and 2.743 \AA for II and III, respectively] than those for the equatorial chlorine atoms [mean $\text{In-Cl}_{(\text{equatorial})} = 2.434$ and 2.424 \AA for II and III, respectively]. The In-In distances are $3.844(1)$ and $3.857(1) \text{ \AA}$, with an In-In-In angle of $121.18(4)^\circ$.

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References

- 1) For a general review see R. L. Wells, *Coord. Chem. Rev.* 1992, **112**, 273.
- 2) R. L. Wells, R. B. Hallock, A. T. McPhail, C. G. Pitt, and J. D. Johansen, *Chem. Mater.* 1991, **3**, 381.
- 3) R. L. Wells, A. T. McPhail, and M. F. Self, *Organometallics* 1992, **11**, 221.
- 4) R. L. Wells, A. T. McPhail, L. J. Jones, M. F. Self, and R. J. Butcher, *Organometallics* 1992, **11**, 2694.
- 5) R. L. Wells, A. T. McPhail, and M. F. Self, *J. Coord. Chem.* 1993, **29**, 27.
- 6) R. L. Wells, A. T. McPhail, L. J. Jones, and M. F. Self, *J. Organomet. Chem.* 1993, **449**, 85.
- 7) R. L. Wells, L. J. Jones, A. T. McPhail, and A. Alvanipour, *Organometallics* 1991, **10**, 2345.
- 8) O. T. Beachley, Jr. and R. N. Rusinko, *Inorg. Chem.* 1979, **18**, 1966.
- 9) Enraf-Nonius Structure Determination Package (SDP 3.0), Enraf-Nonius, Delft, The Netherlands, 1985.
- 10) *International Tables for X-ray Crystallography*; The Kynoch Press, Birmingham, England, 1974, Vol IV.
- 11) J. T. Leman, J. W. Ziller, and A. R. Barron, *Organometallics* 1991, **10**, 1766.
- 12) O. T. Beachley, Jr., E. F. Spiegel, J. P. Kopasz, and R. D. Rogers, *Organometallics* 1989, **8**, 1915.

Figure captions

Fig. 1. ORTEP diagram (40% probability ellipsoids) showing the atom numbering scheme and solid-state conformation of $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$ (I); hydrogen atoms have been omitted. Primed atoms are related to the unprimed atoms by a crystallographic center of symmetry. Selected distances (Å) and angles ($^\circ$), with esd's in parentheses, $\text{In-Cl} = 2.584(3)$, $\text{In-Cl}' = 2.649(3)$, $\text{In-C11} = 2.11(1)$, $\text{In-C21} = 2.11(1)$; $\text{Cl-In-Cl}' = 84.8(1)$, $\text{In-Cl-In}' = 95.2(1)$, $\text{Cl-In-C11} = 103.0(4)$, $\text{Cl-In-C21} = 103.4(4)$, $\text{Cl'-In-C11} = 104.3(3)$, $\text{Cl'-In-C21} = 101.0(3)$, $\text{C11-In-C21} = 144.7(5)$.

Fig. 2. ORTEP diagram (25% probability ellipsoids) of $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$ (II) showing three repeating units and the atom labeling scheme. Primed and double primed atoms are related to the unprimed atoms by crystallographic centers of symmetry. Selected distances (Å) and angles ($^\circ$), with esd's in parentheses: $\text{In1-Cl2} = 2.432(3)$, $\text{In1-Cl2}' = 2.735(2)$, $\text{In1-Cl3} = 2.437(3)$, $\text{In1-Cl3}'' = 2.694(2)$, $\text{In1-C(4)} = 2.11(1)$ Å; $\text{Cl2-In1-Cl2}' = 83.6(1)$, $\text{Cl2-In1-Cl3} = 103.1(1)$, $\text{Cl2-In1-Cl3}'' = 88.0(1)$, $\text{Cl2-In1-Cl4} = 125.1(4)$, $\text{Cl2'-In1-Cl3} = 85.5(1)$, $\text{Cl2'-In-Cl3}'' = 164.0(1)$, $\text{Cl2'-In-C4} = 95.4(3)$, $\text{Cl3-In1-Cl3}'' = 83.1(1)$, $\text{Cl3-In1-C4} = 131.7(4)$, $\text{Cl3''-In1-C4} = 100.6(3)$, $\text{In1-Cl2-In1}' = 96.4(1)$, $\text{In1-Cl3-In}'' = 96.9(1)$.

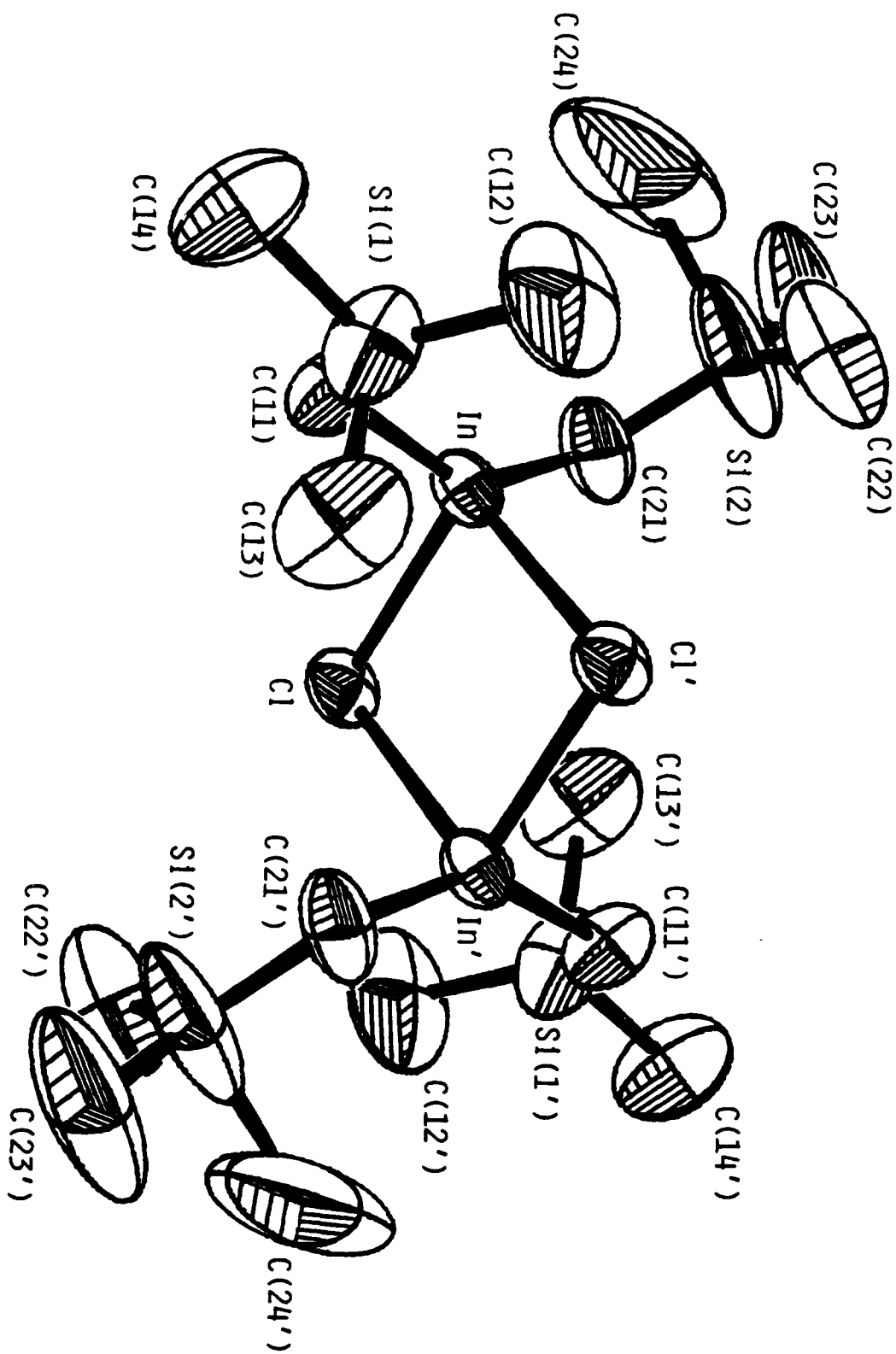


Fig. 1

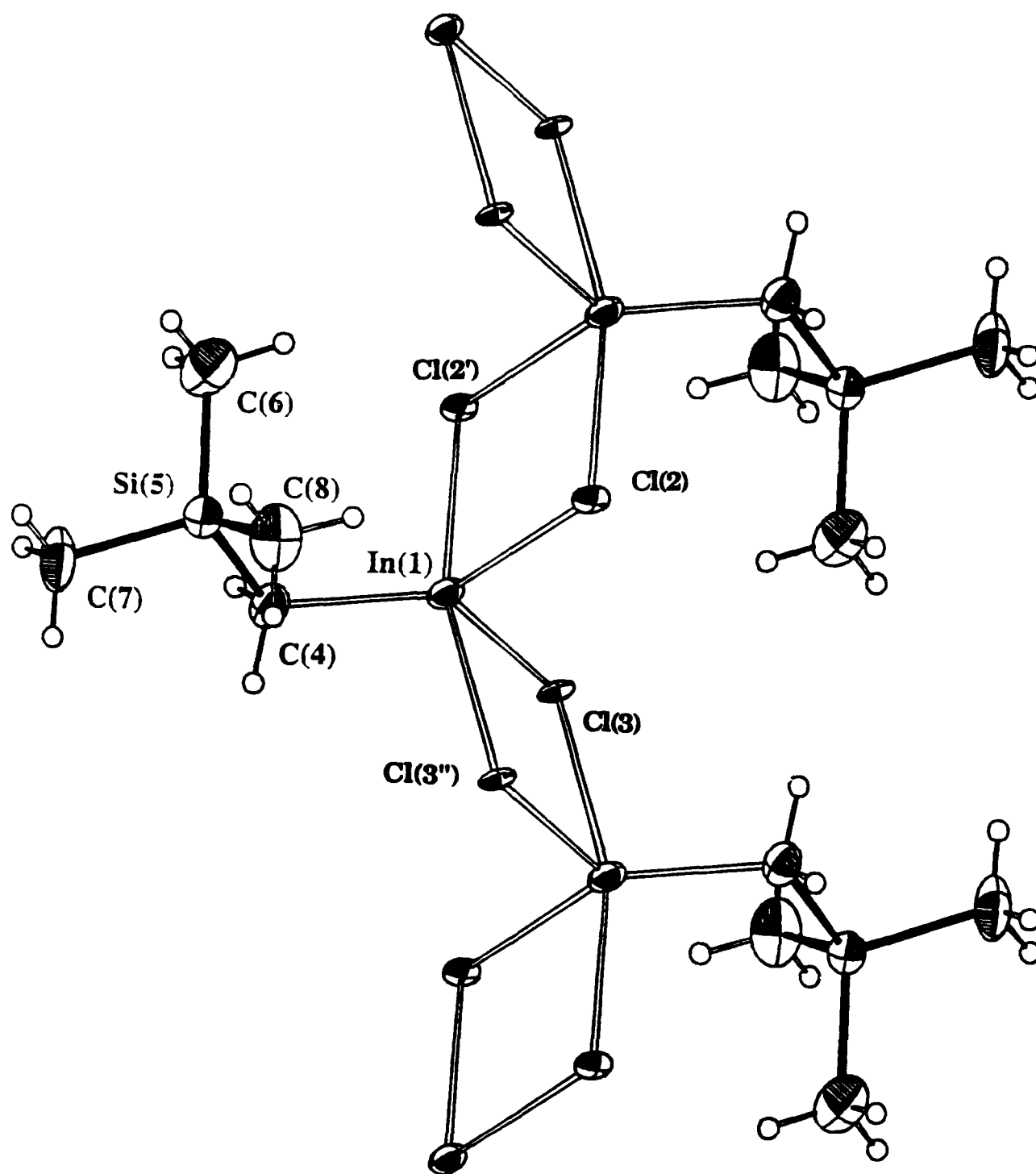


Fig. 2

Table 1. Crystallographic data for $[(\text{Me}_3\text{SiCH}_2)_2\text{InCl}]_2$ (I) and $[(\text{Me}_3\text{SiCH}_2)\text{InCl}_2]_\infty$ (II).

molecular formula	$\text{C}_{16}\text{H}_{44}\text{Cl}_2\text{In}_2\text{Si}_4$	$\text{C}_4\text{H}_{11}\text{Cl}_2\text{InSi}$
formula weight	649.42	272.94
crystal system	triclinic	triclinic
space group	$P\bar{1}(C_i^1) - \text{No.2}$	$P\bar{1}(C_i^1) - \text{No.2}$
$a(\text{\AA})$	10.682(1)	6.708(6)
$b(\text{\AA})$	12.441(1)	12.771(11)
$c(\text{\AA})$	6.141(1)	6.553(5)
$\alpha(^{\circ})$	96.21(1)	96.68(2)
$\beta(^{\circ})$	94.86(1)	116.38(2)
$\gamma(^{\circ})$	75.04(1)	95.56(2)
no. of orientation refls.	25	34
$V(\text{\AA}^3)$	782.4(2)	492(1)
Z	1	2
$D_{\text{calcd.}} (\text{g cm}^{-3})$	1.378	1.841
μ	152	29.6
temp. ($^{\circ}\text{C}$)	25	-171
crystal dimensions (mm)	0.15 x 0.20 x 0.50	0.25 x 0.25 x 0.25
scan type	ω -2 θ	ω -2 θ
scanwidth ($^{\circ}$)	1.15 + 0.14tan θ	2.0 + dispersion
$\theta_{\text{max.}}(^{\circ})$	75	45
intensity control refls.;	2 $\bar{1}$ 2, 1 $\bar{1}$ $\bar{2}$, 3 $\bar{2}$ 1, 3 $\bar{2}$ $\bar{1}$	2 $\bar{1}$ 2, 1 $\bar{1}$ $\bar{2}$, 3 $\bar{2}$ 1, 3 $\bar{2}$ $\bar{1}$
total no. of refls. rec.	3525 (+ h , $\pm k$, $\pm l$)	2169 (+ h , $\pm k$, $\pm l$)
no. of non-equiv.		
refls. rec.	3212	1281
R_{merge}	0.042 (on I)	0.035 (on I)
no. of refls.		
retained	2345 [$I > 3.0\sigma(I)$]	1026 [$F > 2.33\sigma(F)$]
$R (R_w)^a$	0.064 (0.087)	0.036 (0.036)
goodness-of-fit ^b	2.08	0.89
max. shift:esd in final least-squares cycle	0.02	0.04

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$;

$\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized.

^bGoodness-of-fit = $[\Sigma w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

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